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Surfactant removal with multiwalled carbon nanotubes

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ABSTRACT

The ability of multiwalled carbon nanotubes (MWCNTs) to remove a non-ionic surfactant, Triton X-100 (TX100), an anionic surfactant, sodium dodecylbenzenesulonate (SDBS), and a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB) from the aqueous phase was investigated. Untreated, OH-, and COOH-functionalized MWCNTs with different outer diameters and chemical composition were examined and compared. As both the concentrations of surfactants and MWCNTs initially added may affect removal efficiency of surfactants, a relationship between the initial concentration ratio of surfactants and MWCNTs (R_c) and the removal efficiency (E) was established. The results showed that for a given R_c (e.g., 0.8), removal efficiency of the tested surfactants by a specific MWCNT (e.g., the untreated one with outer diameter < 8 nm) decreased in the following order: TX100 (52.3%) > SDBS (26.2%) > CTAB (3.8%). TX100 was more readily removed by MWCNTs than SDBS and CTAB, due to its longer aliphatic chain compared to SDBS and CTAB thus higher hydrophobicity, and stronger π-π interactions with the aromatic structure of the surfaces of

graphite sheets relative to CTAB. Based upon the established relationship between R_c and E of surfactants by MWCNTs, the maximum removal efficiency and the most appropriate R_c of TX100 and SDBS by two MWCNTs (UT8 and OH8) were derived. It was interesting to notice that, except for the case to remove TX100 using UT8, even though a large quantity of UT8 or OH8 was added to the TX100 or SDBS removal systems, they cannot be completely removed, with the maximum removal efficiency in the range of 55.88-87.17%. This mostly resulted from strong aggregation of MWCNTs thus reducing their readily accessible surface area and porosity for sorption.

Key words: surfactant, carbon nanotubes, functionalization, removal efficiency, aggregation

1. Introduction

Surfactants are a group of organic compounds consisting of hydrophilic heads and hydrophobic tails. They have been widely used as detergents, wetting agents, emulsifiers, foaming agents as well as dispersants. The annual global production of surfactants has reached about 13 million metric tons in 2008 (Olkowska et al., 2014). As common constituents in municipal effluents (Petersson et al., 2000), concentrations of surfactants in municipal and industrial wastewaters, especially those from laundries, appear to be very high. Concentrations of linear alkylbenzene sulfonates (LAS), a major contributing anionic surfactant in laundry wastewater, can be as high as 116- 454 mg/L (Ramcharan and Bissessur, 2016). Without undergoing efficient pretreatment, wastewater containing such a high concentration of surfactant may lead to serious environmental consequence once discharged into natural water bodies. For example, a previous study suggested that LAS can exert toxic effect on physella acuta at concentrations above 17 mg/L (Olkowska et al., 2011). In addition, surfactants released into the environment could exert synergistic toxic effects on aquatic organisms in mixtures with other

environmental contaminants (Emmanuel et al., 2005). It is thus of significance and indispensable to find effective ways to remove surfactants once released to water.

Carbon nanotubes (CNTs) have been widely used in many fields due to their unique mechanical, electrical, optical and chemical properties. The applications of CNTs range from composite materials and microelectronics to energy storage and water purification (De Volder et al., 2013). As a result, the production of CNTs from 27 global companies in 2009 has reached 1000 tons, nearly tenfold that in 2004 (Mueller and Nowack, 2008). Theoretically, CNTs have strong adsorbability for organic contaminants due to their large surface area and high hydrophobicity. Previous studies reported that BET surface area of single-walled CNTs (SWCNTs) can reach 3000 m^2/g under the most favorable conditions (Yin et al., 1999). This property makes it possible to mitigate water pollution using CNTs as sorbents. Studies on the interactions between CNTs and environmental contaminants, including organic pollutants such as xylene, dioxin, phenanthrene, naphthalene, bisphenol A, phenol, catechol, and 1-naphthol (Chin et al., 2007; Long and Yang, 2001; Yang et al., 2006; Pan et al., 2008; Liao et al., 2008; Wang et al., 2008; Lin and Xing, 2008), and heavy metals (i.e., Cd^{2+} and Pb^{2+}) (Li et al., 2003; Li et al., 2005), have been done for several years. The results showed that CNTs had unique adsorption properties compared to other carbonaceous materials. For example, the maximum sorption capacity of perfluorooctane sulfonate (PFOS) on MWCNTs with outer diameter < 10 nm was 656 mg/g (Chen et al., 2011), while that of granular activated carbon (Filtrasorb 300) was merely 196.2 mg/g (Ochoa-Herrera and Sierra-Alvarez, 2008). Hence, CNTs is expected to be an ideal sorbent material for surfactant removal. Theoretically, surfactants can be removed well by CNTs, as both of them have hydrophobic and polarizable parts. Besides hydrophobic interaction, some surfactants contain

aromatic structure in their molecules, making π-π electron donor-acceptor interactions another major interaction mechanism because of the π electrons of the benzene rings on the surface of graphite sheets (Chen et al., 2007). Electrostatic interactions may also occur between CNTs and ionic surfactants. Thus, CNTs can adsorb surfactants and remove them efficiently from water.

Previous studies mostly focused on the interaction mechanisms between CNTs and surfactants and their findings demonstrate that CNTs can remove surfactants in water (Bai et al., 2010; Ncibi et al., 2015). However, there is a knowledge gap on how to use the developed theories/mechanisms to remove surfactant from water using CNTs. For example, precise information is lacking regarding the optimal type of CNTs to remove a specific surfactant, the maximum removal efficiency of CNTs, as well as how much CNTs is required for a given surfactant removal system to achieve the maximum removal efficiency at the lowest cost. Although SWCNTs can have a larger surface area, the price of multiwalled CNTs (MWCNTs) is much lower (De Volder et al., 2013), possibly making these the preferred option. Practically, the MWCNTs after surfactant removal can be separated from water with further treating processes, such as with the aid of ultrafiltration techniques (Ma et al., 2016). Hence, in this work, nine kinds of MWCNTs with different outer diameters and functional groups, and three surfactants (i.e., Triton X-100, sodium dodecylbenzenesulonate and hexadecyltrimethylammonium bromide) were chosen to further address surfactant-CNT sorptive interactions. Based on the sorption data analysis, the removal of surfactants by MWCNTs under different conditions was considered to find out which MWCNT is the optimal adsorbent. In this study, we mostly focused on removal efficiencies at various initial concentration ratios of surfactants and MWCNTs, as the initial concentration of both, surfactants and MWCNTs, are important factors that may influence removal

efficiency. Such a relationship can be relevant for assessing the removal efficiencies of surfactants by MWCNTs. By establishing the mathematical equations to describe these relationships, the maximum removal efficiency and the corresponding concentration ratio can be obtained, which is of significance when treating surfactants. With the appropriate amount of MWCNTs that has to be used based upon the concentration ratio of surfactants and MWCNTs, surfactants can be removed adequately and economically. After ultrafiltration to separate MWCNTs from water phase following surfactant removal, the water polluted by the surfactant could be recycled.

2. Material and methods

2.1 MWCNTs and surfactants.

All MWCNTs (purity > 95%) used in this work were purchased from Chengdu Organic Material Co. Ltd., Chinese Academy of Sciences. The untreated and OH-, COOH-functionalized MWCNTs with outer diameters < 8 nm, 20-30 nm and > 50 nm were labeled as UT8, UT30, UT50, OH8, OH30, OH50 and COOH8, COOH30, COOH50, respectively. Surface areas and porosities of all these MWCNTs are described in our previous publications (Zhou et al., 2012; Wang et al., 2010) (Table S1 in the Supplementary Data). A non-ionic surfactant Triton X-100 (TX100), an anionic surfactant sodium dodecylbenzenesulonate (SDBS) and a cationic surfactant hexadecyltrimethylammonium bromide (CTAB) were used as model surfactants and they were all purchased from Sinopharm Chemical Reagent Co., Ltd.. Selected properties of these surfactants are summarized in Table S2.

2.2 Removal efficiency sorption tests

The removal efficiencies of surfactants using MWCNTs were obtained based upon a series of sorption experiments in screwed cap vials with aluminum foil-Teflon liners. Forty milliliters of surfactant

solutions with different concentrations (10-100 mg/L) in Milli-Q water were added to 40 mL vials containing MWCNTs (3-55 mg). The concentrations tested for all surfactants were below their critical micelle concentrations (CMCs) (Table S2). After being mixed on a rotary shaker for 24 h at a speed of 100 rpm, the sorption process was confirmed to have reached equilibrium (Fig. S1 in the Supplementary Data). The samples were then centrifuged at 23,000 rpm with a super-speed centrifuge (Beckman AVANTIJ-301, USA) for 20 min. The residual TX100, SDBS and CTAB in supernatants were quantified with a UV-Visible spectrometer at 225, 235 and 206 nm, respectively. The MWCNT addition and its interaction with surfactant did not change pH values of the surfactant solution (Table S3). This is because no chemical reactions occurred between MWCNTs and surfactants and no acid or alkaline was introduced into the systems. Hence, pH values of the surfactant removal systems were stable during the whole experimental period. Therefore, the systems were not buffered. All supernatants were also examined with UV-Visible spectrometer at 800 nm to make sure that no MWCNTs were present in liquid phase after centrifugation. This approach has been used successfully to determine CNT concentrations (Hyung et al., 2007). All samples were run in duplicate. Since the mass loss of surfactants was less than 2% (Table S4), their uptake by MWCNTs was calculated by mass balance.

2.3 Characterization of MWCNTs

To prepare dry powders of MWCNT-surfactant complexes for obtaining their SEM images, measuring their ζ potential values (ZP) and particle sizes in aqueous phase, all systems in the removal efficiency test were rinsed 2-3 times with Milli-Q water when they had reach equilibrium. The residue was dried in a blast oven for over 24 h at 70 °C. The extracted powders were suspended in Milli-Q water at a

concentration of 10 mg/L, as suspensions at this concentration were appropriate for ζ potential value determination. Suspensions were sonicated for 5 min using a Branson 250 Digital Sonifer at 70% amplitude, and the stable suspensions were immediately measured with a Nano-ZS90 Zeta Sizer (Malvern Instruments Technical Ltd., UK). The pH values of the suspensions were also measured and listed in Table S3.

Aliquots of the extracted powders including complexes of O30-SDBS and O50-SDBS were used to collect SEM images and measure particle sizes in the aqueous phase. Powders were suspended in ethyl alcohol and sonicated for 5 min, then loaded on silicon slices with resistivity of 0.05-0.20 Ω/cm for SEM imaging. SEM images were obtained using a Nova NanoSEM430 (FEI Co., USA). The particle size of O30-SDBS and O50-SDBS complexes in aqueous phase was obtained with a laser particle size analyzer (Beckman, LS13 320, USA). Preparations for this test were done by suspending the extracted powders in Milli-Q water and sonicating for 5 min.

2.4 Data analysis

To compare the difference in removal efficiency of surfactants by various MWCNTs, a relationship between the removal efficiency of surfactant at equilibrium (E) and the concentration ratio of surfactant and MWCNTs initially added to the systems (R_c) was established based on the experimental observations:

$$\boldsymbol{E = E_m \times B / (B + R_c)} \quad (1)$$

where R_c is the concentration ratio of surfactant and MWCNTs initially added to the system; E_m refers to the maximum removal efficiency (%) as R_c is approaching 0, and B is the R_c value when the removal efficiency E reaches 1/2 E_m. The removal efficiency (E) was calculated from the equation E =

100 × (1 - C_e / C_0). Here, C_e and C_0 are equilibrium and initial concentrations of surfactant, respectively.

3. Results and discussion

3.1 Comparison of removal ability

Similar to the previous findings showing that sorption of PAHs (i.e., phenanthrene and naphthalene) and phenolic compounds (i.e., bisphenol A, phenol, and 1-naphthol) by MWCNTs were nonlinear (Yang et al., 2006; Pan et al., 2008; Liao et al., 2008; Wang et al., 2008), sorption of surfactants by the tested MWCNTs was nonlinear as well. This implied that the factors mass of MWCNTs and initial concentration of the chemicals of interests may affect their removal efficiency from the aqueous phase. Thus, the concentration ratio of surfactant and MWCNTs initially added to the systems for removal efficiency tests (R_c) was taken into consideration. A higher R_c value means that at a given concentration of surfactant initially added, a lower amount of MWCNTs is required to reach a specific removal efficiency.

The fitting parameter values of equation 1 for removal of TX100 and SDBS by various MWCNTs are presented in Table 1. It was evident that the results for removing TX100 and SDBS using all nine kinds of MWCNTs can be well fitted with this model, as most R^2 values were above 0.950. In contrast, the results for CTAB can hardly be fitted with this model, as it was shown in the preliminary test that CTAB only showed minimal sorption to all nine kinds of MWCNTs, rendering it challenging to remove CTAB using MWCNTs.

Table 1

To verify that the removal efficiency of CTAB by MWCNTs was very low under any conditions, another series of experiments was set up in 40 mL vials with C_0 (CTAB) = 100 mg/L and mass (MWCNTs) = 5, 30, 55, and 80 mg, respectively. The corresponding four R_c values of CTAB in the systems were calculated as 0.80, 0.13, 0.07, and 0.05, respectively. A comparison of E values correspondingly derived for various R_c values can be used to reflect the differences in removing capability of surfactants by MWCNTs (Fig. 1). Here, R_c = 0.80, 0.13, 0.07 and 0.05 were selected to calculate the corresponding E values with equation 1, making sure that comparisons between all three surfactants were made for the same conditions.

Fig. 1.

The removal efficiency of the tested surfactants using a given MWCNT decreased in the order of TX100 > SDBS > CTAB (Fig. 2). Such an order was applicable for all 9 kinds of MWCNTs at all four R_c levels. The same sorption strength order of TX100, SDBS, and CTAB by only one kind of untreated MWCNTs was observed in a previous study, where the authors mainly focused on the influence of contact time under distinct solid/liquid ratios, initial pH, temperature, and ultrasonication on sorption (Ncibi et al., 2015). As the removing process here was basically a sorption-based process of surfactant molecules towards the MWCNTs, the removal efficiency differences among three surfactants by a specific MWCNT could mainly result from their dissimilar interaction strengths resulting from distinct mechanisms. This was because the chemical structures of the three surfactants tested were quite different from each other. It was reported that organic chemicals can be sorbed to carbon nanoparticles through mechanisms including the hydrophobic effect, π-π bonds, hydrogen bonds, and covalent as well as electrostatic interactions (Yang et al., 2008; Pan and Xing, 2008; Yang and Xing, 2009). The

192 interactions between surfactant molecules and MWCNTs could involve all these mechanisms,
193 depending on the chemical structure of both, the surfactant and MWCNTs under study. The
194 hydrophobic effect is one important driving force leading to sorption, because both the aliphatic
195 carbon chain of the surfactant and outer surface of the MWCNTs are highly hydrophobic. They may
196 attract each other and interact via the hydrophobic interaction mechanism. Besides, for those
197 surfactants with a benzene ring in their molecular structure such as TX100 and SDBS, π-π interaction
198 is also important. Studies focusing on the sorption of aromatic organic chemicals to CNTs have shown
199 that their strong interaction was mainly due to the π-π electron-donor-acceptor (EDA) interaction
200 mechanism between organic molecules and the highly polarizable graphene sheets of CNTs (Chen et
201 al., 2007). Such an interaction process has been demonstrated by spectroscopic studies such as Raman
202 (Gotovac et al., 2007) and nuclear magnetic resonance (NMR) (Chen et al., 2002). The surface of
203 MWCNTs was negatively-charged in Milli-Q water with pH around 7, so there may be electrostatic
204 interactions between the ionic surfactant molecules and MWCNTs (Table S3). Thus, discussion
205 regarding the interaction mechanisms between surfactants and MWCNTs will mainly deal with how
206 the three aforementioned interactions operate in different cases.

207 **Fig. 2.**

208 Compared to the other two surfactants, TX100 can be most readily removed by MWCNTs, up to
209 almost 100%, and in some cases the predicted *E* value for the systems with OH8 added as sorbent
210 material was even over 100% (Fig. 2). High removal efficiency of TX100 was due mainly to its
211 chemical structure. Particularly, TX100 had a long aliphatic carbon chain as well as benzene ring,
212 allowing both strong hydrophobic and π-π interactions. With -OH in its molecular structure, TX100

may act as electron donor and MWCNTs works as electron acceptor in π-π electron-donor-acceptor (EDA) interaction. A predicted *E* value over 100% for the cases with OH8 added means that TX100 can be completely removed if the R_c value was reduced to 0.13 or even lower. This implied that for a given initial concentration of TX100, a large amount of OH8 was added. This could happen under the ideal condition without taking effect of the aggregation of OH8 on its removal efficiency into consideration. This scenario will be further tested and discussed below. For SDBS, π-π electron-donor-acceptor (EDA) interaction may occur with SDBS as electron acceptor because of the $-SO_3$ group in its chemical structure, with MWCNTs acting as electron donor. As the aliphatic carbon chain of SDBS was much shorter than that of TX100, its hydrophobic interaction with MWCNTs was much weaker. Besides, as both MWCNTs and SDBS molecules were negatively charged (Table S3), electrostatic repulsion would have occurred as SDBS molecules were approaching the surfaces of MWCNTs, and this repulsion may have reduced the interaction between SDBS and MWCNTs. However, the repulsion force should be low because ζ potential values of MWCNTs in the SDBS removal systems were relatively low (< -20 mV for most cases) (Table S3). All these factors resulted in 8.9, 12.3, 19.4, and 26.1% lower removal efficiency of SDBS by UT8; 14.8, 23.6, 33.7, and 22.0% by UT30; 32.8, 39.1, 43.8, and 21.7% by UT50; 64.6, 65.0, 62.6, and 30.1% by OH8; 43.6, 43.9, 41.1, and 17.2% by OH30; 11.1, 15.8, 21.6, and 13.6% by OH50; and 37.2, 37.9, 39.2, and 30.6% by COOH8; 23.7, 30.4, 37.4, and 21.4% by COOH30; 35.3, 35.3, 32.7, and 12.9% by COOH50, at the R_c levels of 0.05, 0.07, 0.13, and 0.8, than that of TX100 (Fig. 2). CTAB did not possess a benzene ring, and the length of its aliphatic carbon chain was similar to that of SDBS, making its hydrophobic interaction with MWCNTs relatively weak without the opportunity for π-π interactions. If electrostatic

234 interaction was the dominant mechanism regulating interactions between CTAB and MWCNTs, both
235 the removal efficiency and ζ potential of MWCNTs were supposed to change dramatically within the
236 range of R_c. The reason for this was that the opposite charges of negative for MWCNTs and positive
237 for CTAB would result in a strong attractive force (Table S3). However, our observation showed that
238 the removal efficiencies of CTAB by individual MWCNTs were all very low for the R_c levels
239 investigated. In addition, the ζ potential values of MWCNTs-CTAB complexes also did not show
240 significant changes as CTAB concentration was increased (R_c values were varied from 0.05 to 0.8).
241 Therefore, electrostatic attraction probably was not the predominant sorption mechanism. This can be
242 attributed to the fact that MWCNTs in the CTAB removal systems were weakly charged, with ζ
243 potential value being less than -20 mV for most cases (Table S3). Another possibility was that
244 concentration of CTAB in the systems was relatively low, below its CMC. A previous study regarding
245 sorption of a cationic surfactant on MWCNTs by Wang et al. (2008) showed that their interaction
246 increased most obviously when the surfactant concentration was over its CMC. The interaction
247 between CTAB and MWCNTs could be driven by the relatively weak hydrophobic interactions (Wang
248 et al., 2008). Hence, removal of CTAB with initial concentrations lower than CMC using MWCNTs
249 was much lower than that of TX100 and SDBS. Given the interaction mechanisms between CTAB and
250 MWCNTs as mentioned above, mesoporous carbon could be an alternative option for its removal,
251 because it is highly hydrophobic and can have very large surface area and high porosity.

252 **Fig. 3.**

253 Earlier work has shown that outer diameters of MWCNTs and functional groups are both factors that
254 affect sorption strength of organic chemicals by MWCNTs (Wang et al., 2010). A comparison of R_c

values derived for a specific E value can be used to describe the difference in removal efficiency of the same surfactant by MWCNTs with different outer diameters. To achieve this aim, E = 75%, 50% and 25% were selected to calculate R_c values with equation 1 and the results are shown in Fig. 3. Our observations showed that, generally MWCNTs with smaller outer diameter (i.e., < 8 nm; the UT8, OH8 and COOH8 samples) were more effective in removing TX100 and SDBS relative to those with larger outer diameters at a given E value, due to their larger surface area and porosity (354.0, 569.1, and 350.0 m^2/g in surface area, and 0.91, 1.155, and 0.879 cm^3/g in porosity for UT8, OH8, and COOH8, respectively) (Table S1). MWCNTs with larger surface area can provide more sorption sites for surfactant molecules, facilitating their removal from the aqueous phase. An exception appeared when removing SDBS using OH30 and OH50. It was shown that OH50 had 90.4%, 75.7% and 69.7% higher R_c values correspondingly at the E levels of 75%, 50% and 25% as compared to OH30 (Fig. 3), showing its higher removal efficiency. Such a phenomenon can be ascribed to the stronger aggregation of OH30 in contrast to OH50 in the experimental systems. Although OH50 had smaller surface area, it tended to form smaller aggregates than OH30 did. This can be strongly supported by the difference in SEM images of these two MWCNT-SDBS complexes. Results from particle size tests showed that there was only one peak at 30.07 μm in the aggregates size distribution of OH30, while in the system of OH50 and SDBS, its aggregate size distribution followed a bimodal pattern with two peaks appearing at 18.86 and 76.43 μm, respectively (Fig. 4). A comparison of the predominant peaks of the aggregate size distribution of OH30 and OH50 suggested that, the size of OH30 aggregates was 59.4% higher than that of OH50, which was consistent with the SEM imaging data (Fig. 5).

Fig. 4.

Fig. 5.

Influence of functionalization treatments with hydroxyl and carboxylic groups on removal efficiency of TX100 and SDBS by MWCNTs with a given outer diameter was examined and the results are presented in Fig. 6. It was found that, in most cases, the untreated MWCNTs had higher removing capability for both TX100 and SDBS as compared to the OH- or COOH-functionalized ones with the same outer diameter. This was because grafting polar functional groups to the MWCNTs decreased their hydrophobicity. The water clusters which form at the surfaces of the functionalized MWCNTs through hydrogen bonds with the grafted polar functional groups would reduce accessibility of solute molecules to the solid particles, and the water molecules would strongly compete for the sorption sites with TX100 and SDBS on the functionalized carbon surface (Yang and Xing, 2010). As a result, interactions between surfactant molecules and MWCNTs were strongly inhibited.

Fig. 6.

3.2 Maximum removal efficiency and best mass addition of MWCNTs

To study the relationship between R_c and E, as R_c was reduced from a relatively high value to a value very close to zero, UT8 and OH8 were chosen for further tests as these two kinds of MWCNTs were confirmed to have higher removal efficiencies for both TX100 and SDBS relative to others. To achieve this research aim, different amounts of MWCNTs were added to surfactant solutions at a constant concentration, to ensure that both initial and equilibrium concentrations of surfactants can be measured with UV-visible spectrometer under the experimental condition, as R_c was reduced to a value very close to zero. A mass varying from 3 to 200 mg UT8 and OH8 was added to 40 mL vials, and the initial concentrations of both TX100 and SDBS was 100 mg/L. The results showed that the

297 removal efficiency of these two surfactants increased with decreasing R_c values. This was because of
298 the elevation of their overall surface area and porosity for TX100 and SDBS sorption. However, as R_c
299 was decreased to a certain point, the removal efficiency started to decrease as well (Fig. 7). This can
300 be ascribed to the more pronounced aggregation of MWCNTs (i.e., UT8 and OH8) in the surfactant
301 removal systems at very low R_c levels. As they aggregated, a great number of sorption sites would
302 become inaccessible for the surfactant molecules. Their effectiveness for removing TX100 and SDBS
303 would be reduced accordingly (Fig. 8). Hence, the maximum removal efficiency can be achieved with
304 a proper R_c. The R_c value, related to the maximum removal efficiency (Emax), was defined here as the
305 best added mass concentration ratio of surfactant and MWCNTs (Rba), and it can be applied for
306 practical use of MWCNTs to remove surfactants like TX100 and SDBS in a specific situation. It is
307 possible that the presence of dissolved organic matter (DOM) may affect aggregation of the MWCNTs.
308 However, our previous study showed that, without sonication, no evident suspending was observed
309 while shaking 100 mg/L pristine and COOH-functionalized-MWCNTs for 5 d in the presence of 10
310 mg/L humic acid (Zhou et al., 2012). As the initial concentration of MWCNTs with outer diameters of
311 <10 nm was 200 mg/L, no stably suspended MWCNTs could be clearly detected after shaking with
312 500 mg/L tannic acid under the condition without sonication (Lin and Xing, 2008). It was also
313 reported that MWCNTs could be slightly suspended by DOM without sonication, but the suspended
314 concentration under such condition was quite low. For example, with the initial MWCNT
315 concentration of 500 mg/L, the suspended MWCNT concentration was 17.9 mg/L when treated with
316 200 mg/L of DOM extracted from wheat straw, and 17.2 mg/L when treated with 200 mg/L of DOM
317 extracted from cow manure (Li et al., 2016). It can thus be concluded that the presence of DOM may

not significantly affect aggregation of the MWCNTs thus removal efficiency of the tested surfactants.

Fig. 7.

Fig. 8.

To describe the difference in aggregation of MWCNTs at various R_c values and the associated impact on surfactant removal, a schematic graph is plotted in Fig. 9. The relationship between E and R_c calculated from the experimental results can be described with the modified log normal distribution function and the model-fitting parameters are summarized in Table 2.

$$E = \frac{\mathrm{M}}{R_c} \times e^{-\frac{1}{2}\left[\frac{(\ln R_c - \ln \mathrm{Q})}{\mathrm{n}}\right]^2} \quad (2)$$

Here, M is the removal coefficient (dimensionless); Q is an index to describe the outer diameter of MWCNTs and an increase in Q means the outer diameter of the MWCNTs increases. The parameter n reflects the dispersion of MWCNTs in the surfactant removal systems. The physical meaning of these three parameters is derived from the procedures as presented in the Supplementary Data (Fig. S2). To test the possibility of over-parameterization on goodness of data fitting, the mean weighted square error (MWSE) of the equations with different parameter numbers was calculated and compared. Details are described in the Supplementary Data (Table S5). This method has successfully been used in our previous study to identify suitable model parameterizations (Shen et al., 2015).

Fig. 9.

For a given concentration of surfactant (C_s) and water volume (V), the best mass addition of MWCNTs (Mba) can be calculated with the equation Mba = C_s×V/Rba. Here, Rba refers to the best added mass concentration ratio of surfactant and MWCNTs as mentioned before. The relationship

between R_c and E described by equation 2 may also exist between other CNTs and surfactants, as long as the concentration of surfactant is below its CMC. Therefore, Mba of any CNTs for removing diverse surfactants may be determined according to equation 2. However, the related parameter values could be case-dependent. With the optimal added mass concentration ratio, surfactant can be removed most efficiently with the lowest cost using CNTs. It was interesting to note that, except for the case of removing TX100 using UT8, even though a large amount of UT8 or OH8 was added to the TX100 or SDBS removal systems, they cannot be completely removed, with Emax ranging in 55.88-87.17% (Table 2). This was mostly due to strong aggregation of MWCNTs thus reducing their effective surface area and porosity available for sorption.

Table 2

4. Conclusions

Surfactants with a long aliphatic carbon chain and benzene ring (TX100 and SDBS) can be readily removed using MWCNTs because of their strong hydrophobic interaction and π-π interaction. The MWCNTs with smaller outer diameters had higher removing capability of both non-ionic and anionic surfactants (e.g., TX100 and SDBS) relative to those with larger diameters, and the untreated MWCNTs performed better than the OH-, and COOH-functionalized ones. Thus, MWCNTs with smaller outer diameters are very effective in surfactant removal in water, especially those with longer aliphatic carbon chain and aromatic structure. For a given MWCNT and surfactant, the removal efficiency (E) was mainly determined by the mass concentration ratio of surfactant and MWCNTs present in the systems (R_c). The relationship between E and R_c derived in the present work can provide useful guidance for estimation of the appropriate amount of CNTs that is required for surfactant

359 removal using CNTs, ensuring it can be removed completely and economically. The findings from this
360 study are of great significance for making up strategies for surfactant removal using carbon
361 nanomaterials. One has to be aware that, the real wastewater most likely contains diverse
362 compositions (e.g., organic pollutants and heavy metals, DOM, and other unknown constituents),
363 which may complicate the interactions between surfactants and MWCNTs and influence the removal
364 efficiency of surfactants. The impacts and the associated underlying mechanisms can be studied in
365 future work. The findings from this laboratory work may provide basic information and a scientific
366 foundation for the future engineering applications of MWCNTs for real wastewater treatment.

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372 **Appendix A. Supplementary data**

373 Supplementary data related to this article can be found at http://dx.doi.org/10.1016/

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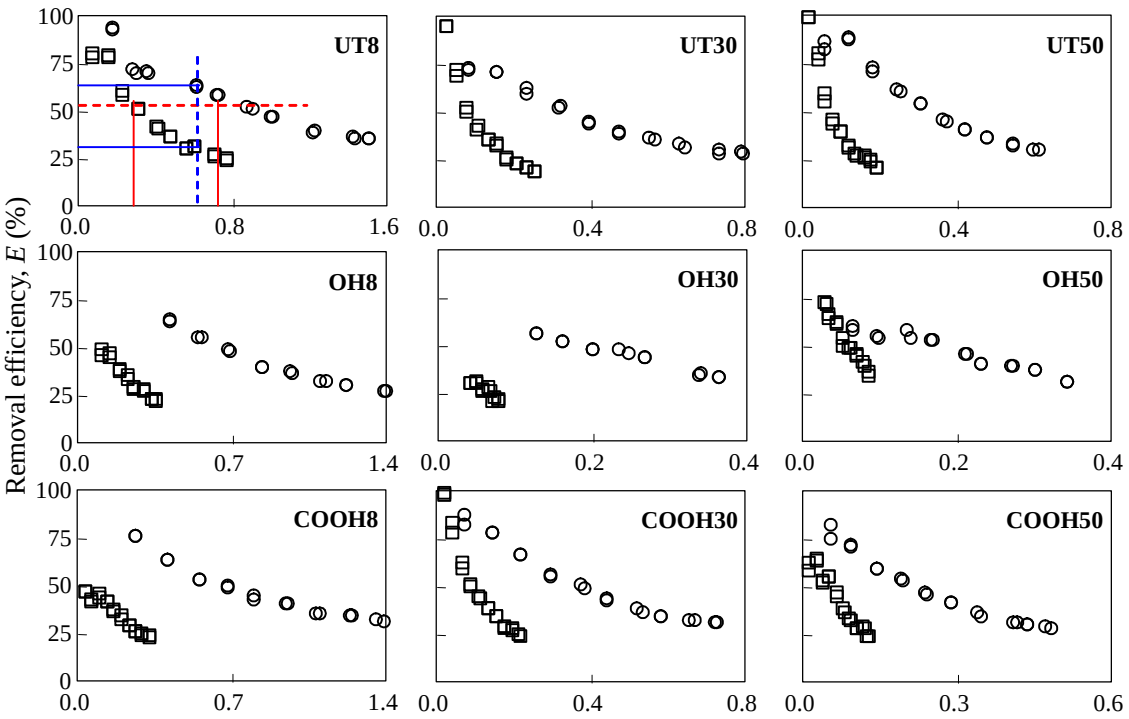

Fig. 1. The relationship between E and R_c values for removal of TX100 (○) and SDBS (□) using various MWCNTs. Here, E is a calculated value, and there is no error bar for it at a specific R_c value. The E value decreases with increasing R_c values, and theoretically it will nonlinearly drop to zero as R_c approaches infinity. This means that surfactants may not be removed if no MWCNTs are added to the systems.

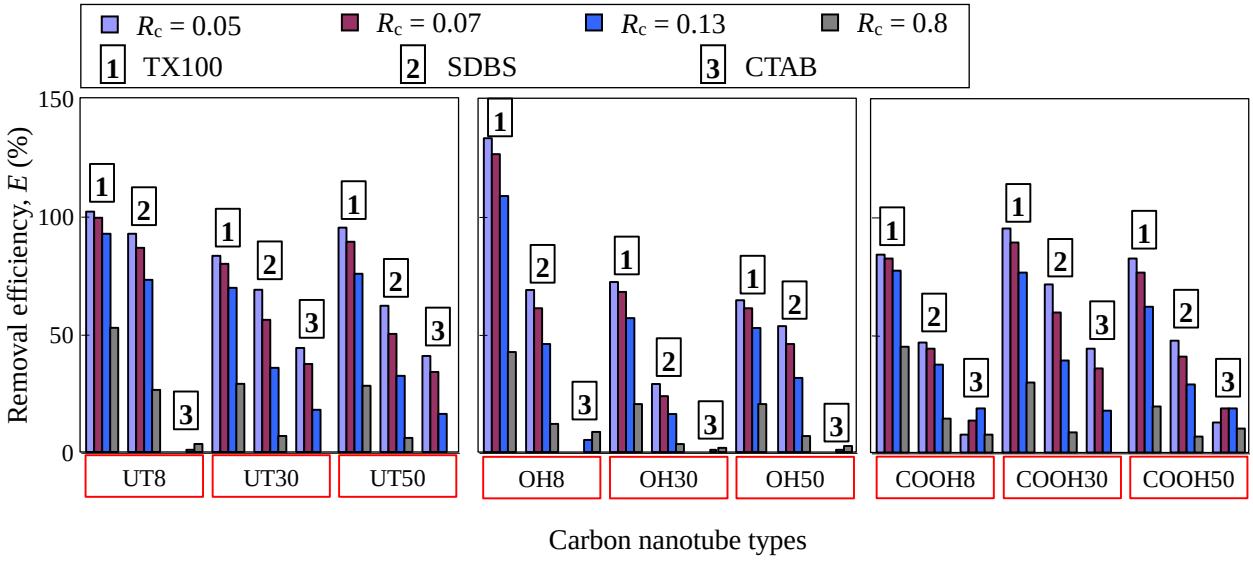

Fig. 2. The removal efficiencies (E, %) of TX100, SDBS, and CATB by various carbon nanotubes at different R_c values.

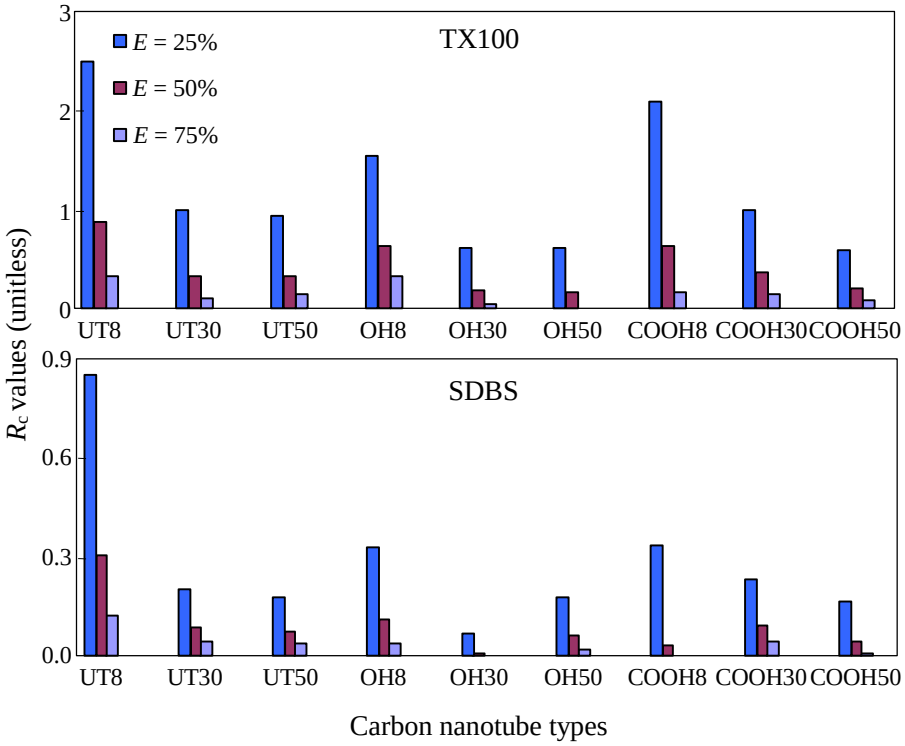

Fig. 3. A comparison of removal ability of MWCNTs with the same functional group but different outer diameters. The R_c values correspond to the removal efficiencies of TX100 and SDBS by various carbon nanotubes at the E levels of 25%, 50% and 75%.

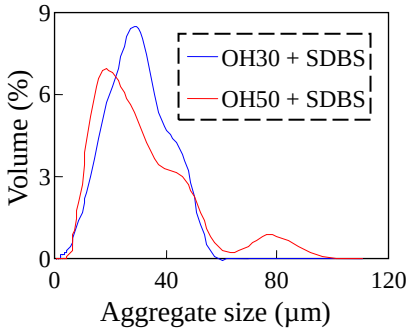

Fig. 4. The aggregate size of OH30 and OH50 in the SDBS removal systems.

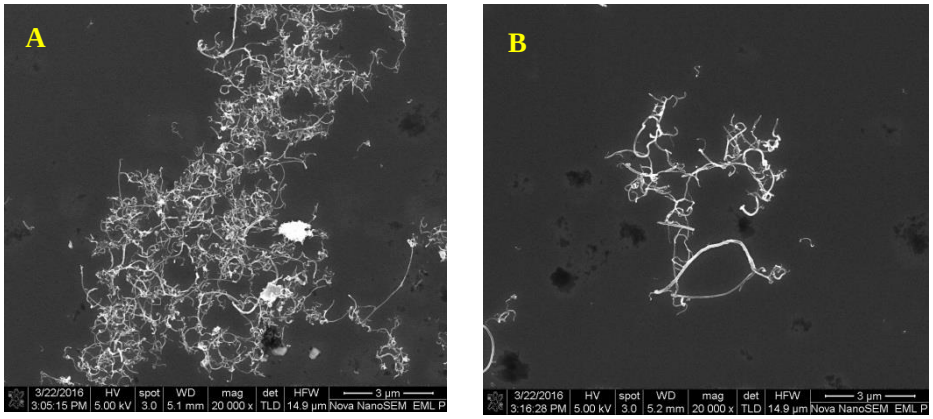

Fig. 5. SEM images of (A) OH30-SDBS complex and (B) OH50-SDBS complex.

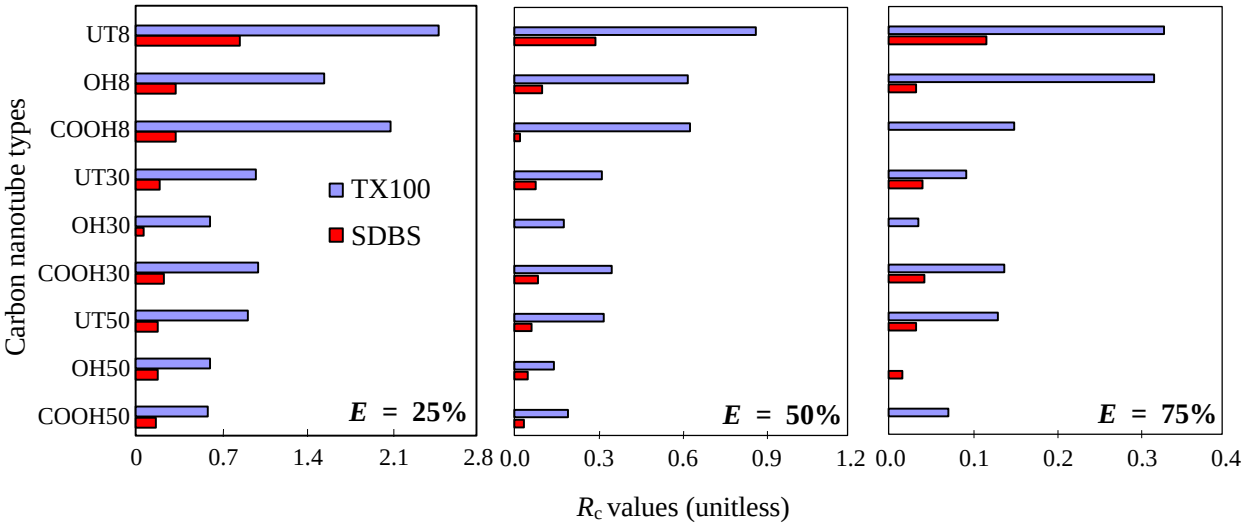

Fig. 6. A comparison of the removal capability of TX100 and SDBS by individual MWCNTs with the same outer diameter but different functional groups at removal efficiencies of 25%, 50% and 75%.

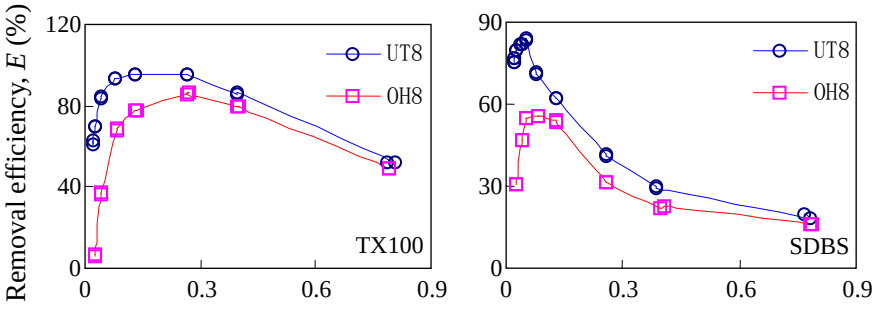

Fig. 7. The relationship between E and R_c values for removal of TX100 and SDBS using UT8 and OH8.

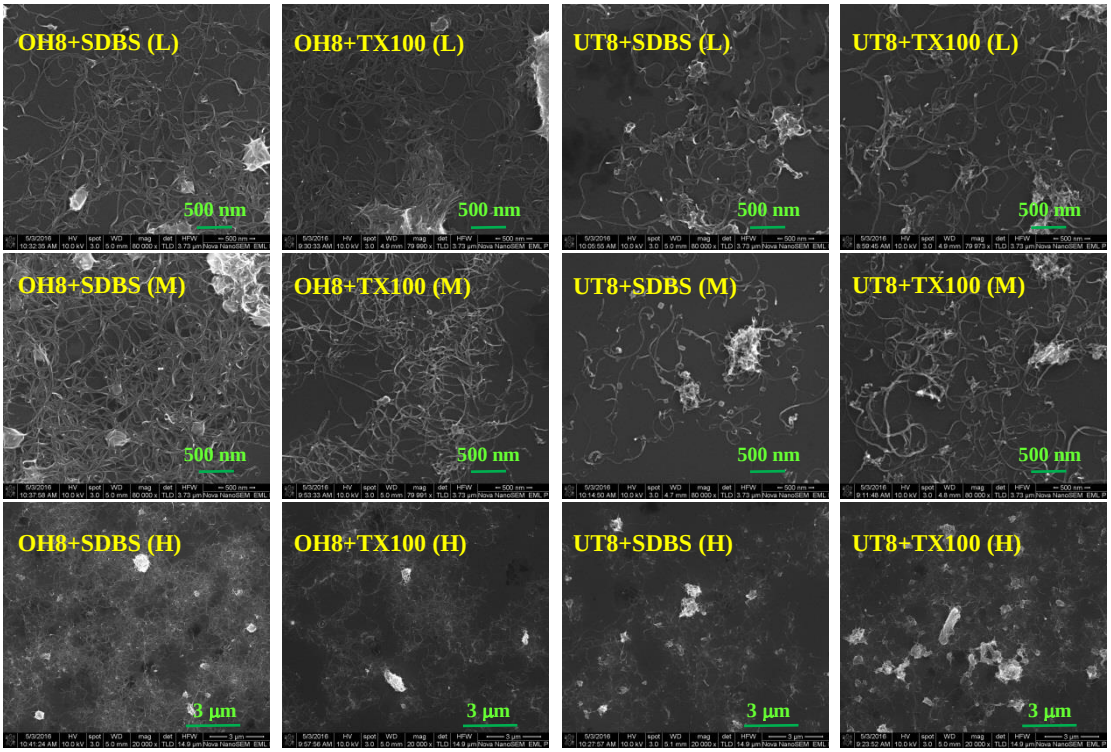

Fig. 8. The SEM images of UT8 and OH8 showing their aggregation at various R_c values. Here L, M, and H refer to the added amount of MWCNTs at low, medium, and high levels, respectively. They correspond to the R_c levels at high, medium, and low levels, respectively.

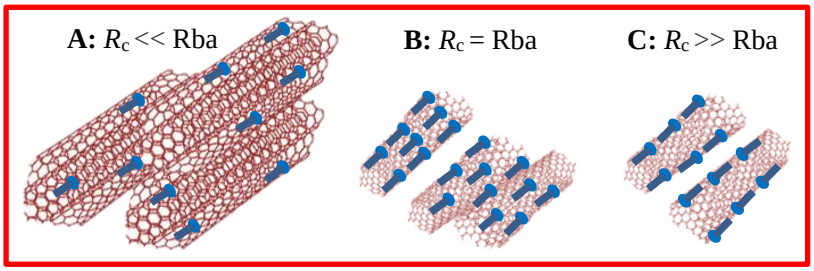

Fig. 9. A schematic graph showing aggregation of CNTs and surfactant removal efficiency at various R_c levels. Rba refers to the best added mass concentration ratio of surfactant and MWCNTs. At this R_c point, removal efficiency of the surfactant by MWCNTs is the highest (B). As R_c is much higher than Rba, removal efficiency of the surfactant is quite low. This is because in this case, although the MWCNTs added to the systems are highly dispersed, there are not so many sites on MWCNTs for surfactant sorption (C). In comparison, as R_c is far below Rba, which means that the amount of MWCNTs added is excessive, they may become highly aggregated thereby strongly reducing removal efficiency of the surfactant (A).

Table 1

The model-fitting parameters for removal of TX100 and SDBS using various MWCNTs.

Removal systems	E_m (%)	B	R^2
UT8+TX100	108.3±3.9[a]	0.747±0.065[b]	0.962
UT30+TX100	95.0±3.3	0.356±0.028	0.995
UT50+TX100	113.2±6.2	0.262±0.032	0.994
OH8+TX100	156.0±6.2	0.295±0.017	0.996
OH30+TX100	86.7±4.7	0.249±0.029	0.958
OH50+TX100	75.6±3.8	0.297±0.041	0.897
COOH8+TX100	89.0±4.4	0.814±0.102	0.914
COOH30+TX100	110.8±3.3	0.292±0.019	0.981
COOH50+TX100	104.7±2.5	0.185±0.010	0.988
UT8+SDBS	111.5±6.1	0.245±0.028	0.952
UT30+SDBS	158.6±5.6	0.038±0.002	0.992
UT50+SDBS	154.9±6.4	0.034±0.003	0.986
OH8+SDBS	100.4±11.6	0.109±0.020	0.946
OH30+SDBS	58.0±11.3	0.049±0.018	0.786
OH50+SDBS	98.6±7.0	0.060±0.010	0.877
COOH8+SDBS	55.0±2.3	0.280±0.034	0.950
COOH30+SDBS	142.8±3.9	0.049±0.003	0.992
COOH50+SDBS	78.5±4.9	0.076±0.012	0.876

[a, b]: standard errors of E_m and B. The R^2 for removal of SDBS by OH30 is slightly below 0.8, with a value of 0.786. This is because sorption strength of this surfactant by OH30 is relatively low. A few data points are slightly scattered. All other fittings are good.

Table 2

The model-fitting parameter values of equation 2 along with the maximum removal efficiency (Emax) and the corresponding best added mass concentration ratio (Rba) for various removal test systems.

Systems	M	n	Q	R^2	Rba	Emax
UT8+TX100	62.40±8.09	1.81±0.07	3.25±0.87	0.935	0.123	98.79
OH8+TX100	41.25±2.14	1.27±0.04	1.06±0.11	0.978	0.211	87.17
UT8+SDBS	12.46±0.55	1.68±0.04	0.63±0.07	0.993	0.037	81.11
OH8+SDBS	9.41±0.57	1.16±0.06	0.33±0.04	0.944	0.086	55.88

Surfactant removal with multiwalled carbon nanotubes

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Supplementary Data

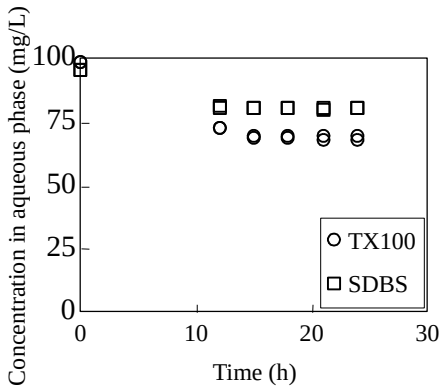


Fig. S1. The sorption equilibrium time for TX100 and SDBS by UT8. Since sorption strength and equilibrium time of these two surfactants by UT8 were higher than other CNTs used, they were shown here as examples.

Physical meaning of parameters used in equation 2

$$E = \frac{\mathrm{M}}{R_{\mathrm{c}}} \times e^{-\frac{1}{2}\left[\frac{(\ln R_{\mathrm{c}} - \ln \mathrm{Q})}{\mathrm{n}}\right]^2}$$

Since *M* is directly proportional to *E*, it can be defined as the removal coefficient of surfactant.

Taking the UT8+TX100 system as an example, if we fix M and *n* in equation 2, but vary Q from 3.5, to 4.0, and finally to 5.0. It is clear that shape of the curve may not change, but the removal efficiency of surfactant would decrease at a specific R_c value (Fig. S2-A). It can thus be concluded that Q is an index to describe the outer diameter of MWCNTs. With an increase in Q, the outer diameter of the MWCNTs increases. Consistently, surface area and porosity of the MWCNTs decrease, so the removal efficiency (*E*) of surfactant would decrease.

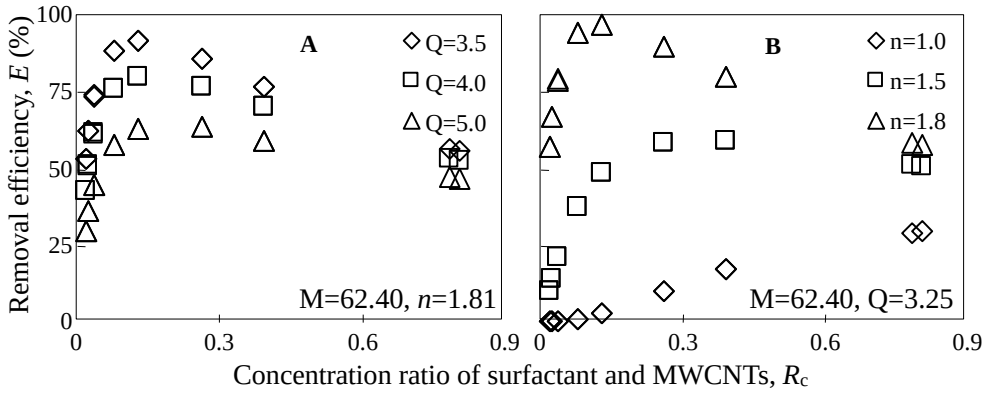


Fig. S2. Effect of the Q and *n* changes on removal efficiency of surfactant (*E*).

In this equation, if we fix M and Q, the curve would inevitably pass the point (Q, M/Q), whatever the *n* takes. When R_c is lower than Q, the magnitude of *n* may determine the shape of the curve. Particularly, if we increase the *n* value from 1.0 to 1.5, and finally to 1.8, the removal efficiency of surfactant (e.g., TX100) increases at a specific R_c (Fig. S2-B). It can thus be concluded that the parameter *n* can be an index to describe the dispersion of MWCNTs in the surfactant removal systems. The system with a higher *n* value means that the MWCNTs used would aggregate at a lower R_c value, implying that the MWCNTs disperse better thus reaching a higher removal efficiency.

Table S1

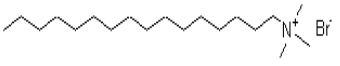
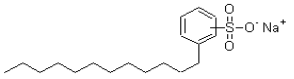
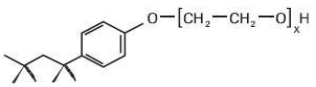
Surface area and porosity of the untreated, OH-, and COOH-functionalized MWCNTs.

Carbon nanotubes	SA (m^2/g)	V_{mic} (cm^3/g)	$V_{mes + mac}$ (cm^3/g)
UT8	354.0	0.230	0.680
UT30	133.9	0.088	0.391
UT50	76.5	0.064	0.155
OH8	569.1	0.255	0.900
OH30	130.4	0.074	1.169
OH50	77.1	0.054	0.696
COOH8	350.0	0.186	0.693
COOH30	130.8	0.081	0.338
COOH50	76.2	0.047	0.194

SA: surface area; V_{mic}: micropore volume; $V_{mes + mac}$: a sum of meso- and macropore volume.

Table S2

Selected properties of the surfactants used in this study.

Surfactant	Molecular formula	Molecular weight (g/mol)	CMC (mg/L)	Molecular structure
CTAB	$CH_3(CH_2)_{15}N(CH_3)_3Br$	364	291.2[a]	
SDBS	$CH_3(CH_2)_{11}COO_6H_4NaO_3S$	348	870[b]	
TX100	$C_{14}H_{22}O(C_2H_4O)_{9.5}$	625	150[c]	

[a,b,c] from Lin et al. (2010)

Table S3

Zeta potential values of the original MWCNTs and MWCNT-surfactant complexes in the surfactant removal efficiency test systems.

Samples	Zeta potential (mV)	pH	Samples	Zeta potential (mV)	pH
			SDBS		7.41
UT8	-12.6	6.68	UT8-SDBS	-35.7	7.38
UT30	-13.7	6.68	UT30-SDBS	-36.6	7.42
UT50	-12.8	6.65	UT50-SDBS	-38.2	7.41
OH8	-18.9	6.59	OH8-SDBS	-36.1	7.45
OH30	-21.6	6.58	OH30-SDBS	-34.9	7.33
OH50	-19.0	6.65	OH50-SDBS	-35.2	7.39
COOH8	-19.6	6.56	COOH8-SDBS	-37.2	7.42
COOH30	-18.1	6.62	COOH30-SDBS	-33.8	7.32
COOH50	-18.2	6.56	COOH50-SDBS	-34.9	7.39
TX100		6.78	CTAB		6.79
UT8-TX100	-20.0	6.89	UT8-CTAB (R_c = 0.05)	33.5	6.84
UT30-TX100	-20.4	6.79	UT8-CTAB (R_c = 0.07)	38.1	6.81
UT50-TX100	-27.5	6.92	UT8-CTAB (R_c = 0.13)	39.3	6.82
OH8-TX100	-22.7	6.73	UT8-CTAB (R_c = 0.80)	44.3	6.81
OH30-TX100	-23.5	6.76	OH8-CTAB (R_c = 0.05)	35.6	6.87
OH50-TX100	-27.4	6.75	OH8-CTAB (R_c = 0.07)	37.8	6.84
COOH8-TX100	-21.0	6.60	OH8-CTAB (R_c = 0.13)	44.1	6.82
COOH30-TX100	-22.3	6.79	OH8-CTAB (R_c = 0.80)	42.0	6.88
COOH50-TX100	-25.5	6.67	COOH8-CTAB (R_c = 0.05)	41.1	6.78
			COOH8-CTAB (R_c = 0.07)	42.7	6.75
			COOH8-CTAB (R_c = 0.13)	46.6	6.79
			COOH8-CTAB (R_c = 0.80)	47.1	6.75

Table S4

Mass loss of TX100 and SDBS before and after shaking.

Surfactants	Concentration before shaking (mg/L)	Concentration after shaking (mg/L)	Mass loss (%)
TX100	97.4	96.5	0.90
SDBS	82.3	81.2	1.30

The over-parameterization test

Apart from equation 2 in the main text, one additional model with two parameters (Q and *n*) was used to fit the relationship between R_c and E.

As the number of parameters in two models is different, it is necessary to test whether the parameter number of 3 used in equation 2 is overparameterized. To achieve this aim, the mean weighted square error (MWSEs) for each model was calculated using the formula as below and compared.

$$\mathrm{MWSE} = \frac{1}{\upsilon}\sum_{i=1}^{N}[(\mathrm{E}_{\text{measured-i}} - \mathrm{E}_{\text{model-i}})^2 / \mathrm{E}^2_{\text{measured-i}}] \quad \text{(S1)}$$

In equation S1, v is the degree of freedom (v = N-3 for equation 2 in the main text, and v = N-2 for the second model with two parameters "Q and *n*" in Table S5); N is the number of experimental data points; i represents a data point with a certain E; $\mathrm{E}_{\text{measured-i}}$ is the ith measured removal efficiency at equilibrium, and $\mathrm{E}_{\text{model-i}}$ is the ith estimated removal efficiency at equilibrium (Shen et al., 2015).

It is evident that the MWSE values for equation 2 are two orders of magnitude lower than the other model and the fitting parameters are in a reasonable range, instead of being a value of infinity (inf) for all cases. Hence, to get a reliable relationship between E and R_c, at least three parameters are required.

Table S5

The model-fitting parameters of equations 2 in the main text and another one with two parameters Q and *n* along with the MWSE values in each test system under different models.

Equations	Systems	M	*n*	Q	R^2	MWSE
$E = \frac{\mathrm{M}}{R_c} \times e^{-\frac{1}{2}[\frac{(\ln R_c - \ln \mathrm{Q})}{\mathrm{n}}]^2}$	UT8+TX100	62.40±8.09	1.81±0.07	3.25±0.87	0.935	0.004
	OH8+TX100	41.25±2.14	1.27±0.04	1.06±0.11	0.978	0.002
	UT8+SDBS	12.46±0.55	1.68±0.04	0.63±0.07	0.993	0.004
	OH8+SDBS	9.41±0.57	1.16±0.06	0.33±0.04	0.944	0.005
$E = \frac{1}{R_c} \times e^{-\frac{1}{2}[\frac{(\ln R_c - \ln \mathrm{Q})}{\mathrm{n}}]^2}$	UT8+TX100		8.87E08±inf	8.65E-06±inf	0	0.736
	OH8+TX100		1.26E09±inf	5.10E-03±inf	0	0.880
	UT8+SDBS		8.03E08±inf	7.17E04±inf	0	0.617
	OH8+SDBS		1.34E08±inf	0.129±inf	0	0.794

References

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